Green Deep Eutectic Solvents for Pulp and Papermaking Industry

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SUMMARY
The study into preparation and characterization of cellulose prepared by deep eutectic solvents (DES) facilitate a deeper understanding of their favourable characteristics such as low cost of preparation, environmentally-friendly and high degree of cellulose dissolution that show great potential as cost-effective and sustainable solution in the pulping process for papermaking industries. Herein the conference paper, we compare the effectiveness of biomass fractionation using alkaline treatment to shadow kraft process and using prepared choline chloride (ChCl)/urea binary DES. The treated cellulosic fibers are then characterized with Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction and Scanning Electrion Microscopy (SEM) to investigate possible difference in their physicochemical properties. From the study, it was found that molar ratio of 1:2 for ChCl/urea DES was most suitable for the treatment of biomass due to its lower viscosity and hence ease of mixing that would lower cost in industrial scale.

KEYWORDS
Cellulose, Deep Eutectic Solvent, Paper, Pulping, Water

INTRODUCTION
The world is facing a grim environmental issue arising from the over-usage of water in industrial activities, which calls for the quest to develop sustainable industrial process with blue footprints. The global paper and pulp market size has been forecasted to increase from USD 63,300 million in 2019 to USD 86,700 million in 2025[1]. In this regard, we delve into the study and application of deep eutectic solvents in the pulping process for papermaking. Figure 1 illustrates the schematic flow of conventional Kraft pulping and paper milling processes; It is estimated that one A4 sized paper uses 20 L of water to produce in the conventional processes[2].

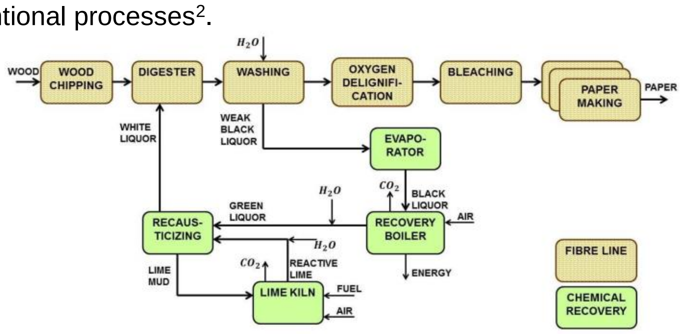

Figure 1: Process flow of conventional Kraft pulping and paper milling

The presence of lignin and hemicellulose creates a protective structure around the cellulose fibers in the woody biomass, contributing to hydrolytic stability via their ester and ether linkages; This provides the cell wall with the strength to remain in structured form[3]. However, this eventually leads to biomass recalcitrance where the cellulose has low accessibility due to the high lignin content[4]. In order to successfully derive cellulose fiber, the raw lignocellulosic biomass requires mechanical treatment such as wood chipping with high shear to reduce their size before chemical pre-treatment for the purpose of fractionating cellulose out of the biomass[5].

Deep eutectic solvents (DESs) are considered a new generation of ionic liquids that eliminates the high cost of preparation and are both non-toxic and environmentally-friendly. To date, limited literature reports and knowledge is available to have a clear understanding of the cellulose dissolution ability in DESs[6]. By customizing the molar ratio of binary components in the DES, the physicochemical properties could be altered and designed according to needs. This paper works on treating the biomass with eutectic mixture of choline chloride (ChCl) and urea prepared in 1:2 molar ratio, having melting point of 12 ^{o}C; Choline chloride acting as the hydrogen bond acceptor while the latter as the donor having melting points of 302 ^{o}C and 133 ^{o}C in their individual state respectively[7-8].

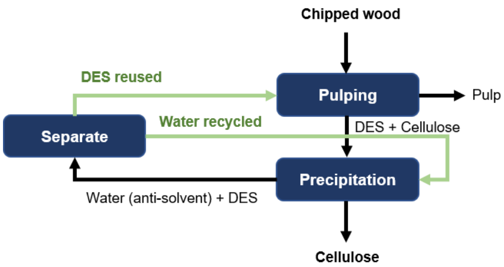

Figure 2: Proposed process of pulping incorporated with DES

This conference paper first demonstrates the preparation of ChCl/urea DES at different molar ratios. Thereafter, comprehensive comparison of effectiveness of cellulose pulp treatment with alkaline and DES will be discussed. Finally, the characterization of physicochemical properties of the cellulose fiber prepared would be manifested.

MATERIALS AND METHODS

Materials

Rice husks were purchased from Far East Flora, washed, dried, grinded and sieved through 355 µm mesh size. Sodium hydroxide, pearl (99 – 100 %), Choline Chloride (≥ 98 %) and Urea (≥ 99.5 %) were purchased from Sigma Aldrich Pte. Ltd. (Singapore). Analytical grade Hydrogen Peroxide (30 – 32 %) was purchased QReC®. Analytical grade Acetic acid, glacial was purchased from VWR Singapore.

Alkaline treatment of ground rice husk

5 g of ground rice husk was added to 250 mL of 5 % (w/w) NaOH and stirred vigorously at 90 ^{o}C for 1.5 hours. At the end of the reaction, the suspension was filtered and centrifuged with deionized water until near neutral pH. Then the treated pulp was dried in oven at 70 ^{o}C overnight.

Preparation of DES

Approximately 50 g of ChCl/urea DESs were prepared with molar ratios of 1:2, 1:4, 1:6 and 1:8 individually. They were produced by mixing under stirring at 450 rpm at 80 ^{o}C for 2.5 hours to obtain a clear mixture. The DESs were prepared under moisture-free environment.

DES treatment of ground rice husk

The treatment with ChCl/urea DES was carried out by adding 5 g of ground rice husk into 50 g of DES that was preheated to 100 ^{o}C for 3 hours. The solution was stirred at 400 rpm during the dissolution. Thereafter, 200 mL of deionized water was added, and the resulting suspension was vacuum filtered. The solid was washed 8 times with 100 mL water each time. The filtered residue was dried in air-circulated oven at 70 ^{o}C overnight.

Bleaching of treated pulps

Peracetic acid was prepared by mixing 50 % acetic acid, 38 % H_2O_2 and 12 % deionized water. The Alkaline-treated and DES-treated pulps were individually added to 250 mL of peracetic acid and stirred vigorously at 70 ^{o}C for 3 hours and constant slow mixing overnight. After that, the suspension was vacuum filtered and washed in centrifuge until pH becomes near neutral. The bleached samples were dried in vacuum oven at 70 ^{o}C overnight.

Characterization of bleached pulps

Chemical composition was determined by FTIR, that was analysed using Shimadzu IRPrestige-21 with 45 scans per spectrum, covering wavenumber range of 400 – 4000 cm^{-1}. The degree of crystallinity could be analysed with XRD analysis using Bruker D8 Advance, collected over 2Ө angles from 5 – 50^{o}, at scanning rate of 2^{o}/min. Finally, JEOL JSM-6701F Field Emission SEM (FESEM) was used to study the morphologies of the treated and bleached cellulosic samples.

RESULTS AND DISCUSSION

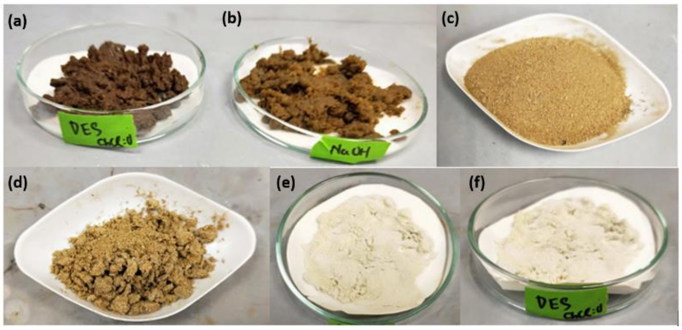

Figure 3: Pictures of **(a)** Wet DES-treated rice husk, **(b)** Wet alkaline-treated rice husk, **(c)** Dried ground DES-treated rice husk, **(d)** Dried ground alkaline-treated rice husk, **(e)** Dried bleached alkaline-treated cellulose fiber and **(f)** Dried bleached DES-treated cellulose fiber

The samples were well characterized by FTIR, XRD and FESEM, exhibiting effectiveness of preparation of pure cellulosic fiber with green and selective ChCl/urea deep eutectic solvents.

CONCLUSIONS

It has been established that molar ratio 1:2 Choline chloride/urea DES could be utilized for the dissolution of cellulose in biomass. Upon characterization and analysis, it has been established that the ChCl/urea DES could replace the prevalent Kraft treatment in the pulping process. The selective dissolution and precipitation of pure cellulosic fiber was investigated and was proven to be a water conserving process by capability of recovering and recycling water loop in comparison with Kraft treatment.

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